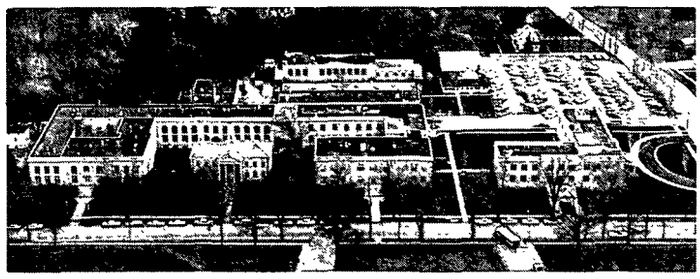

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LOCALIZED CORROSION OF STAINLESS STEELS IN PAPER MACHINE WHITE WATER

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Introduction

The paper industry must comply with requirements for pollution-free effluents by 1985. This demands either sophisticated and expensive clarification systems or reuse of mill process streams. The advantages are overwhelmingly in favor of water reuse in the paper mill (1). Among the problems created by closing up paper machine white water systems, corrosion is of great concern. The change in white water corrosivity caused by closure and ensuing damage to mill equipment by corrosion have been the subject of previous papers (2, 3). To combat this problem, the current trend in our industry is a change to all stainless steel construction. Thus, it is important to understand how white water, changed by closure, affects the severity of stainless steel corrosion.

From a corrosion standpoint, the important environmental conditions which are changed by closure are the type and amount of dissolved solids build-up, higher temperature, and increased biological activity. More difficult pH control, the amount and type of organic compounds, and dissolved gases are also considered to be important environmental influences on corrosion in closed systems. In the localized corrosion of stainless steel, the most damaging inorganic dissolved species is the chloride ion, but its effect is modified by the presence of other anions (3, 4). Higher white water temperatures decrease corrosion resistance as will be shown later. In locations of lower temperature, recycled white water is nutritious for bacteria growth. Bacteria accelerate the kinetics of localized corrosion, also shown later in this report. It now appears that dissolved organic compounds

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influence localized corrosion. In white water from bleached furnish, these probably originate from carbohydrate, starch, dye, and resinous substances. In addition to these compounds, white water from unbleached stock may also contain spent liquor and lignin type organic constituents (5, 6). The exact identity and role of those organic species which contribute to the initiation and/or propagation of localized attack on stainless steel is yet to be determined. There is also limited information on the effect of dissolved gases on corrosion in recycled paper machine white water (7).

The two most common stainless steels used in paper machine construction and repair are AISI Types 304 and 316. Currently, the low carbon grades of these alloys, 304L and 316L, are more popular. In either case, these metals are subject to localized attack in the form of pitting and crevice corrosion. Corrosion of these grades of stainless steel in the form of pitting has been identified in several paper machine components, e.g., headboxes, foil support boxes, couch rolls (8, 9). In these cases, the cause of pitting attack was ascribed to changes in the white water environment and machine operating conditions or to the condition of the metal (metallurgical or surface) as installed or repaired. Paper machine corrosion in the form of crevice attack frequently occurs beneath fibrous deposits.

Our research efforts are directed toward the determination of the severity of these two forms of corrosion caused by the aforementioned changes in white water properties or conditions as a result of closure. The purpose of this paper is to present the results of localized corrosion tests on Type 304 and 316L stainless steel in white water of various compositions, temperature, and biological activity. Preliminary test results are given relative to improvements in corrosion resistance as a result of polishing and/or passivating the stainless steel surfaces.

Experimental

Polarization tests were used to evaluate the resistance of both metals toward pitting in both real and simulated white water of various compositions. All tests were conducted at a scan rate of 0.6 v./hr. using saturated calomel as reference and platinum as counter electrodes.

Deposit corrosion tests were conducted by measuring the applied anodic potential necessary to activate corrosion beneath a deposit which was clamped on the stainless steel plate surface. The test apparatus for these tests has been described previously (2, 3). It is shown in Figures 1 and 2.

The chemical composition and mechanical properties of the stainless steel test specimens are shown in Figure 3. All plate specimens were ground to 120 grit finish, degreased with toluene, and ultrasonically cleaned prior to tests. In one series of tests, the plates were either passivated as ground or passivated after electropolishing. The procedure for this passivation treatment is shown in Figure 4.

Discussion of Results

In the evaluation of dissolved (inorganic) solids build-up, the importance of sulfate/chloride concentration on localized corrosion of Types 304 and 316L stainless steel was reviewed previously. Margin of safety values for pitting and deposit corrosion were defined. These measurements were used to analyze the corrosivity of simulated white water as a function of SO_4/Cl ratio, pH, and total dissolved solids (inorganic) (3).

The margin of safety for pitting corrosion is defined graphically in Figure 5. This value for deposit corrosion is the sum of the open circuit potential, regardless of sign, and the applied anodic potential indicated by a continuous rise in current, as follows:

M.S.(deposit) = O.C. Potential + Activation Potential

Effect of Temperature

In both real and simulated waters covering a pH range from 4.2 to 6.85 and a wide range of dissolved solids, a temperature rise from 27 to 71°C caused a more rapid activation of deposit corrosion on Type 304 stainless steel. This effect is more pronounced in higher pH waters (Figure 6).

Effect of Biological Activity

Biological activity accelerated by both innoculation and stagnant conditions did not cause crevice corrosion on either metal in tests of two weeks duration. In fact, when the crevice was activated by applied anodic potential, the resulting corrosion products annihilated "the bugs." However, severe corrosion damage was found in all areas of slime and fiber deposits once the corrosion process was activated (Figure 7).

Evaluation of Real White Water and Effect of Dissolved Organic Compounds

The results from the complete battery of corrosion tests on ten real white waters compare very favorably with our results on simulated waters both from the standpoint of concentration and type of dissolved solids. These data are current and still being evaluated. In the evaluation of real white water samples, there seems to be a correlation between the level of dissolved organic compounds and the activation of deposit corrosion (Figure 8). The level of organics indicated in these data originates primarily from stock contaminants and lignin compounds as the tested white water was from unbleached stock. Similar correlations were found in NCASI's* corrosion results between color and uniform corrosion rate of mild steel (10). The exact type and role of organic compounds in the white water which influences localized

*NCASI — National Council of the Paper Industry for Air and Stream Improvement.

corrosion processes is currently under investigation. It is interesting to note, however, that the very low margin of safety value indicated for Type 304 in Mill Number 5 white water was not due to corrosion beneath the deposit. Rather, it was the result of deposit formation from the water on the free area of the test specimen as shown in Figure 9. The severe crevice corrosion attack associated with these very reactive deposits was in the form of smooth hemispherical craters as shown in Figure 10.

Similar deposit formation was not found on Type 316L stainless steel. The water was analyzed for biological activity and it was found to be very low. Long term exposure tests in this water on both metals showed active pitting on 304 and none on 316L. Thus, accelerated deposit formation on the 304 alloy is associated with early pit formation.

Effect of Dissolved Gases

The effect of lowering the dissolved oxygen from 8 to 1 ppm had the expected result of reducing the pitting potential and the range of passivation on both metals by approximately 150 mv, S.C.E. Further work is required to evaluate this effect on crevice corrosion as well as the effect of dissolved CO_2 and H_2S on both corrosion processes. Preliminary results for two levels of carbonate/CO_2 concentration are shown in Figure 11. No significant difference is indicated at these levels for this relatively nonaggressive, simulated white water.

Future Work

The white water study for the immediate future will primarily involve the evaluation of two corrosion control measures; namely, improved surface condition of the metal and inhibition. Metal surface treatments will include polishing and passivation. Inhibition involves changes in white water quality, e.g., clarification treatments and/or additives which render stainless steel surfaces immune from attack by aggressive species in the white water.

Tests on ground and electropolished stainless steel plates which have been passivated by the procedure shown in Figure 4 are currently underway. Preliminary test results in simulated white water containing various SO_4:Cl concentrations are shown in Figure 12. The results do not show any substantial improvements in corrosion resistance from the polishing-passivation treatment, particularly in the more aggressive solutions. This is probably due to metallurgical quality of the test materials as the location of attack, either in the pitting or deposit test, preferred local, microdefects in the polished surface regardless of imposed crevices. Thus, it appears that surface finish condition influences deposit formation more than the activation of corrosion beneath deposits which are already present. More work is planned in this program using metals of better metallurgical quality.

References

1. Bush, S. W., TAPPI Papermakers Conference Proceedings, Atlanta, April 10-12, 1978, pp. 121-124.

2. Bowers, D. F., Tappi, V. 60, No. 10, p. 57, October, 1977.

3. Ibid., V. 61, No. 3, p. 57, March, 1978.

4. Uhlig, H. H., and Leckie, H. P., Journal Electrochemical Society, V. 113, No. 12, p. 1262, December, 1966.

5. Easty, D., Institute of Paper Chemistry, Private Communication.

6. Dugal, H. S., Institute of Paper Chemistry, Private Communication.

7. Morgeli, B., Canadian Pulp & Paper Industries, February 5, 1978, p. 23.

8. Private Communication and Consultation, IPC member companies.

9. Mueller, W. A., and Muhonen, J. M., Tappi, V. 55, No. 4, p. 589, April, 1972.

10. McCourt, J. E., Jr., NCASI, Private Communication.

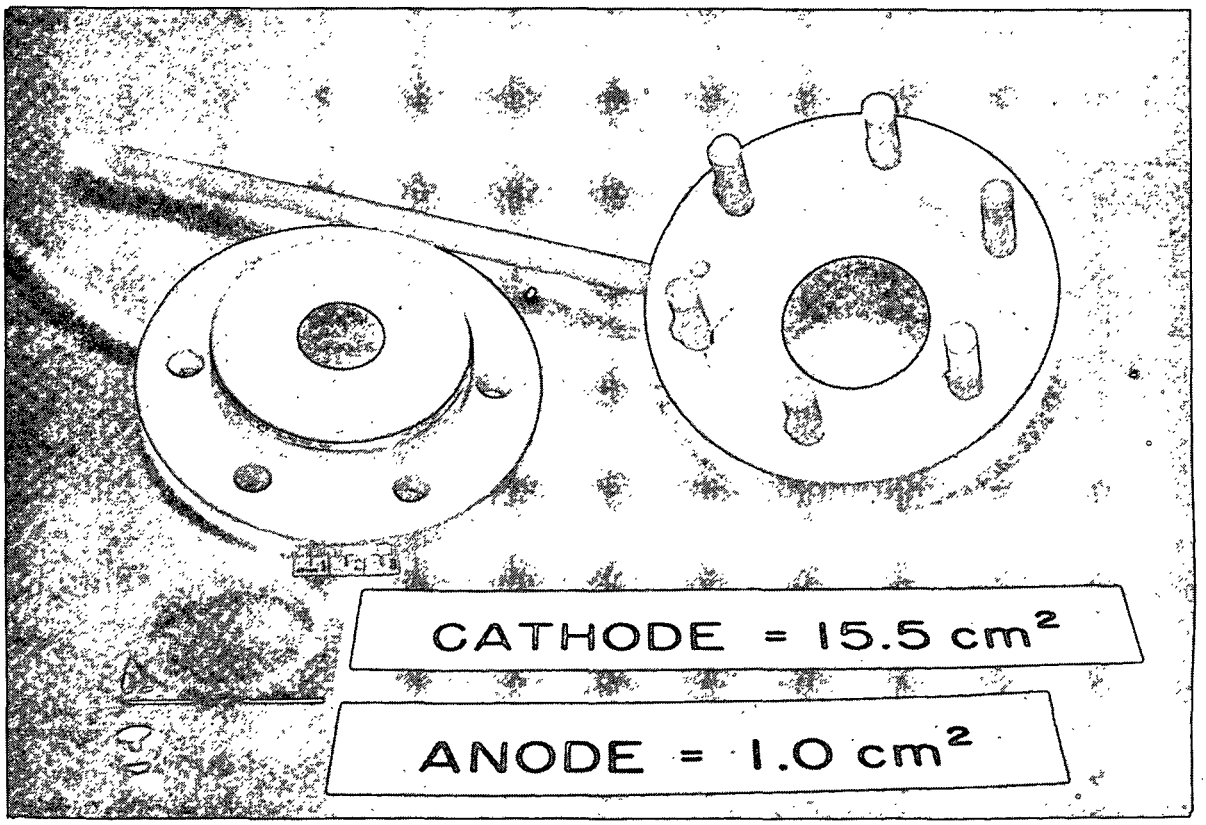

Figure 1. Test Apparatus Used in Deposit Corrosion Tests, Unassembled

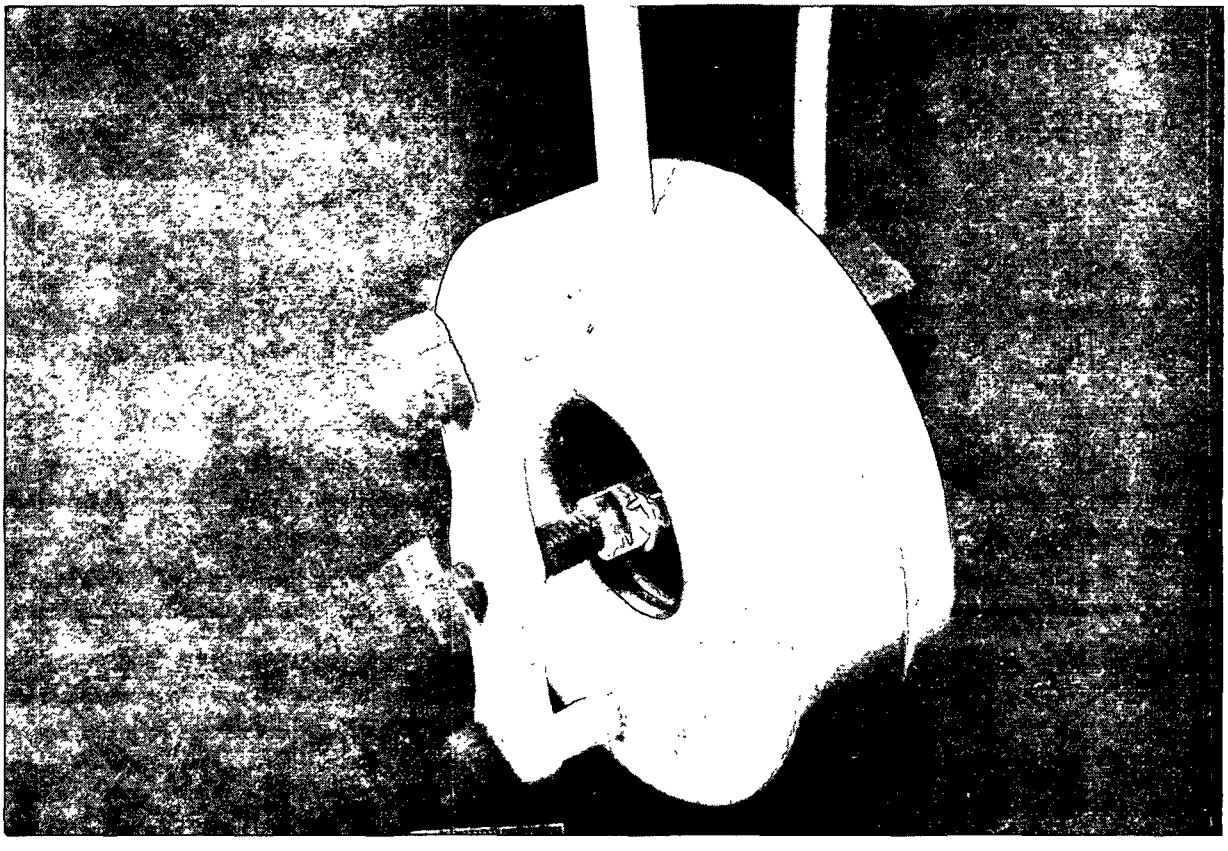

Figure 2. Test Apparatus Used in Deposit Corrosion Tests, Assembled

Chemical Composition

Type Metal	C	MN	Si	P	S	Ni	Cr	MO
304	0.07	1.52	0.53	0.026	0.015	9.05	19.28	0.33
316L	0.020	1.61	0.58	0.023	0.016	11.30	17.16	2.44

Mechanical Properties

Type Metal	Tensile	Yield	Elongation	Hardness
304	88940	39450	61.0	RB84
316L	86400	41200	44.0	RB85

Figure 3. Stainless Steel Test Specimens

1. 10% Phosphoric Acid Rinse
2. Cold Water Rinse
3. 30-40 Minutes in 20% HNO_3 at 49-60°C
4. Cold Water Rinse
5. Hot Water Rinse
6. Air Dry — Still or Forced

Figure 4. Passivation Treatment for Stainless Steel (ASTMF-86 Modified)

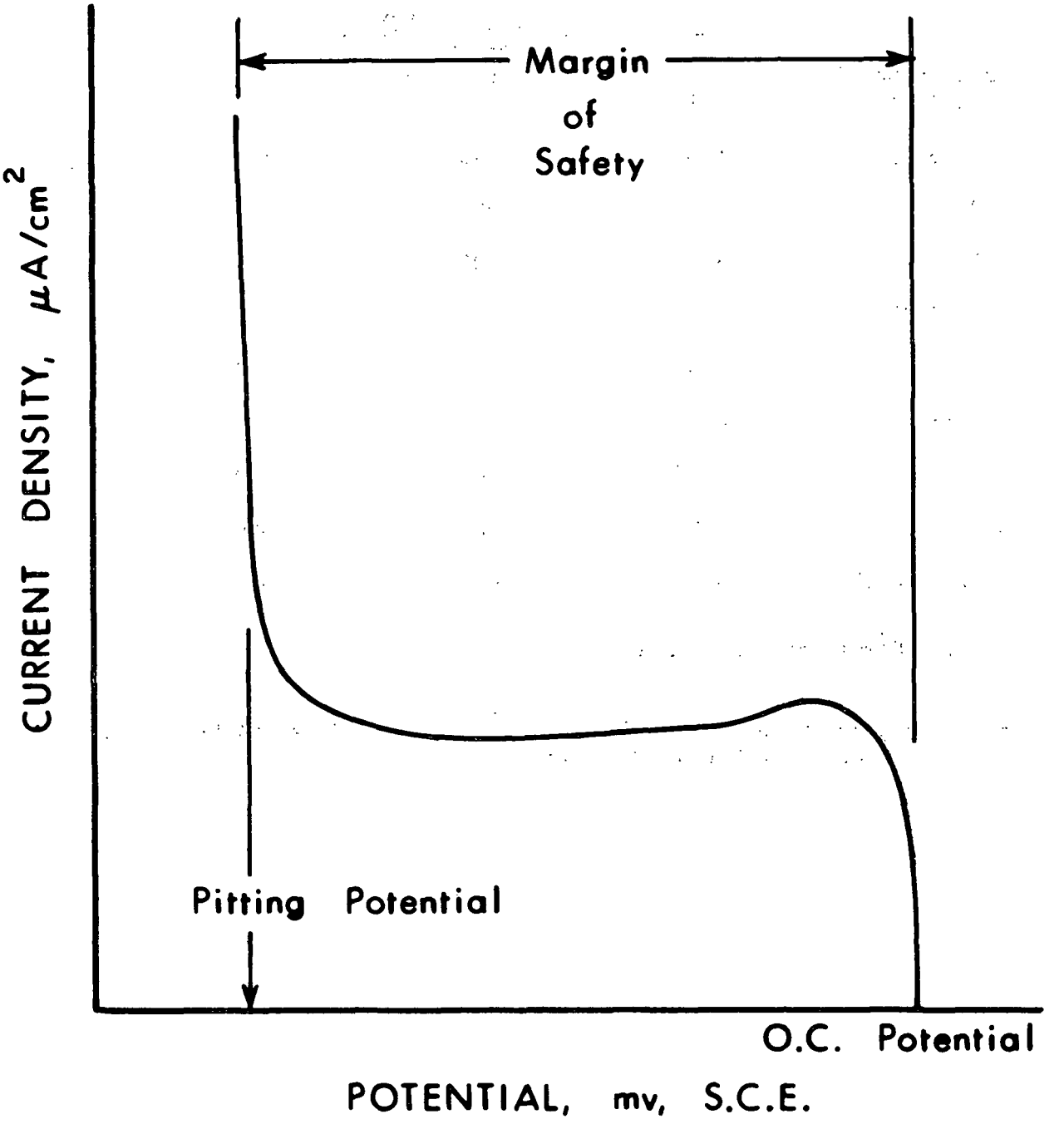

Figure 5. Graphical Illustration of Schematic Anodic Polarization Curve for Type 304 and 316L Stainless Which Defines the Margin of Safety (mv., S.C.E.) for Pitting Corrosion

Mill Number and (pH)	Temperature (°C) 27	Operating Temperature (37-48)	71
1 (5.6)	480	440	420
2 (5.7)	760	980	600
3 (6.0)	820	800	580
4 (6.3)	780	580	500
5 (6.3)	680	840	520
6 (6.5)	680	660	500
7 (6.8)	600	565	440
Sim. 50 (5.9)*	720	720	380
Sim. 5 (4.3)*	520	640	340

*Sim. = Simulated white water.

Figure 6. Margin of Safety for Deposit Corrosion Type 304 Stainless Steel at Various Temperatures

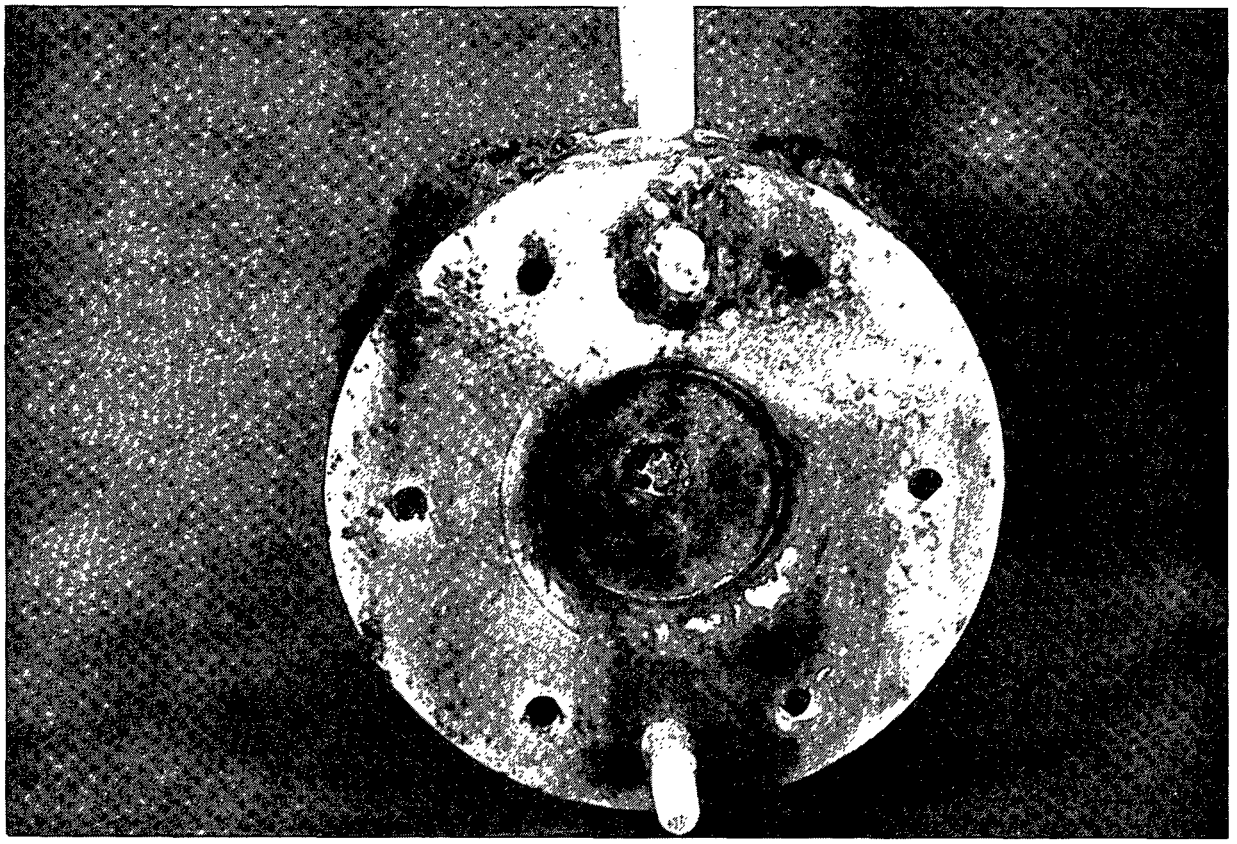

Figure 7. Photograph Showing Severe Crevice Corrosion Attack in the Presence of Sulfate Reducing Bacteria

Mill Number	Dissolved Solids Volatile (ppm)	Deposit Margin of Safety Type 304	Type 316L
1	140	980	580
2	180	565	535
3	500	580	600
4	580	585	600
5	660	20	300
6	830	300	260

Figure 8. Margin of Safety Deposit Corrosion Types 304 and 316L Stainless Steel at Various Organic Dissolved Solids Levels

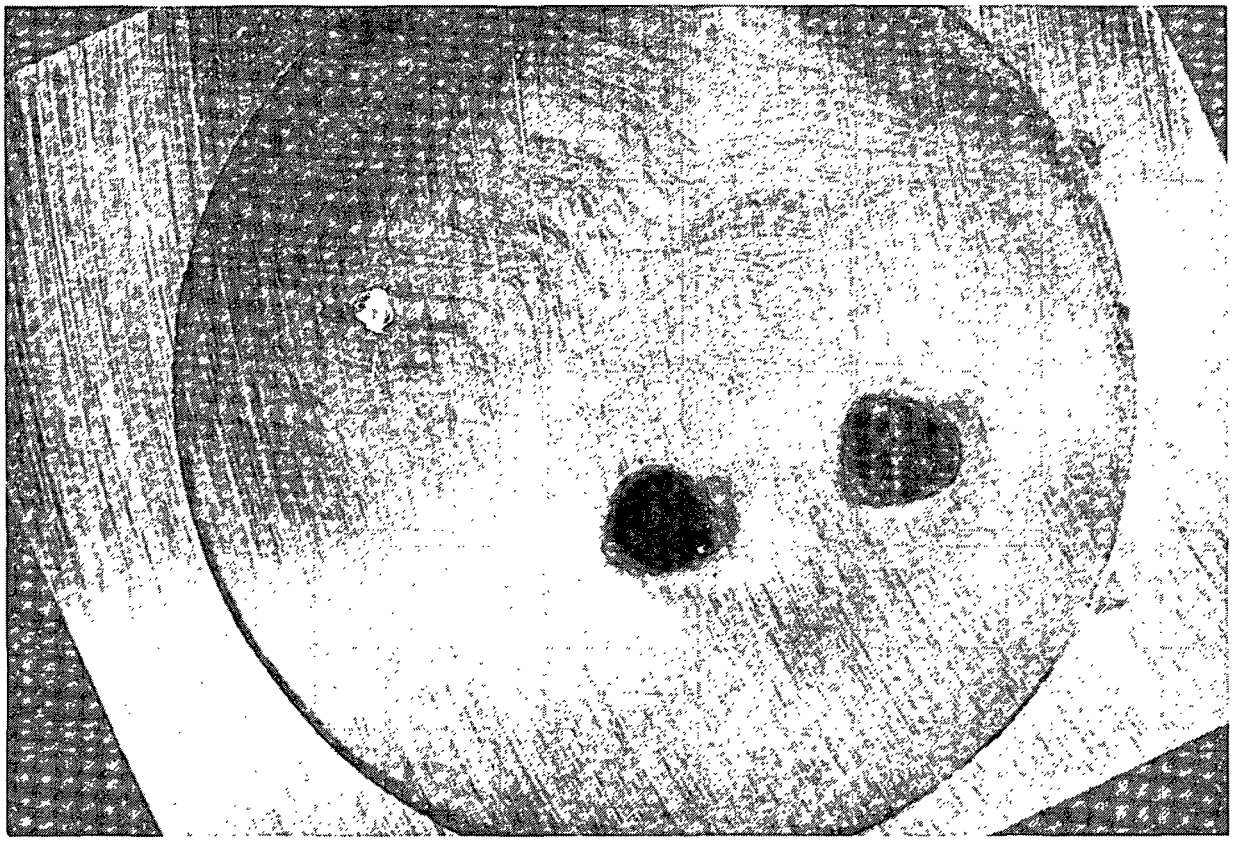

Figure 9. Photograph Showing Deposit Formation on Type 304 Stainless Steel From Mill Number 5 White Water Early in the Deposit Corrosion Test

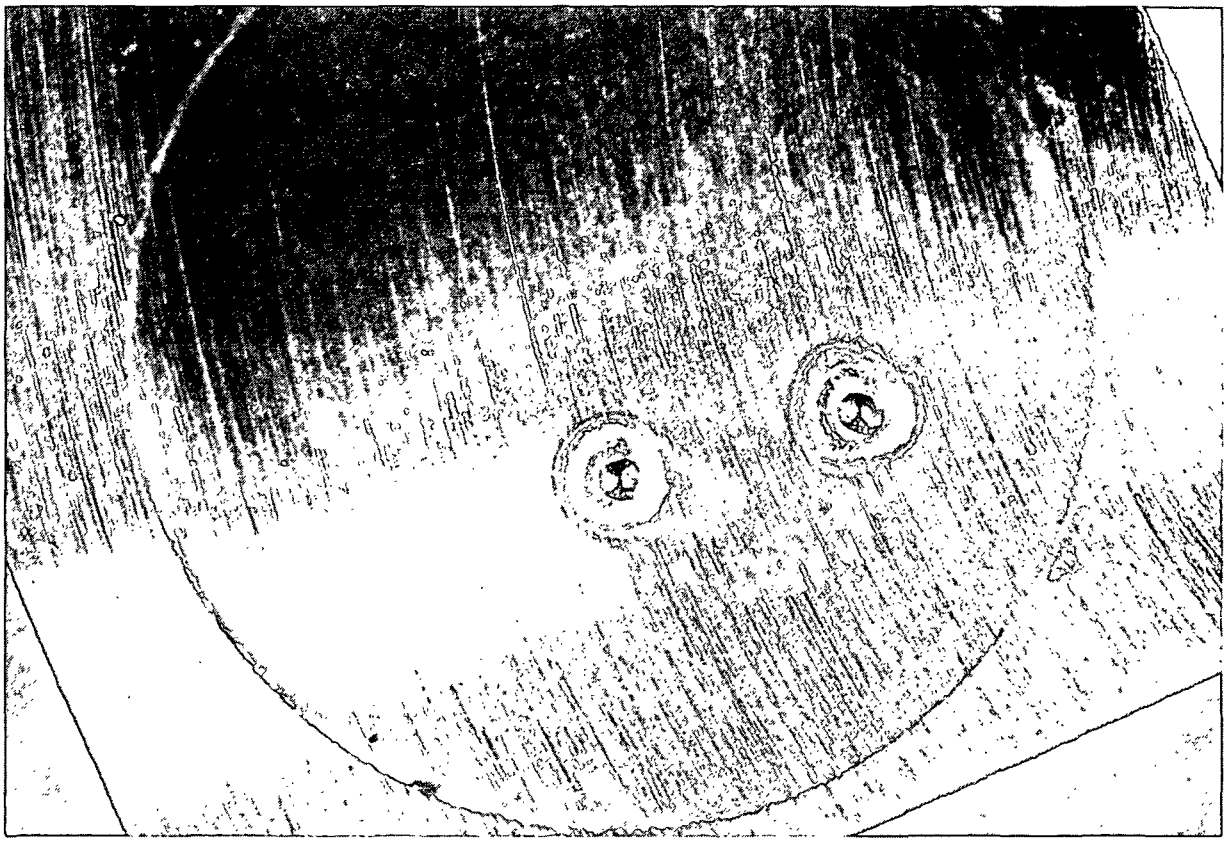

Figure 10. Same as Figure 9 Showing the Smooth Hemispherical Craters Beneath the Water Formed Deposits

Solution*	Pitting M.S. 304	Pitting M.S. 316L	Deposit M.S. 304	Deposit M.S. 316L
50 ppm CO_3^{-2} 3.78 pH	1160	1160	>1000	>1000
50 ppm CO_3^{-2} 6.40 pH	1000	1000	>1000	>1000
250 ppm CO_3^{-2} 3.58 pH	1160	1180	>1000	>1000
250 ppm CO_3^{-2} 6.60 pH	1000	940	--	>1000

*Solution — Simulated white water, 5000 ppm, total dissolved solids, 10:1, SO_4:Cl.

Figure 11. Margin of Safety M.S., (mv., S.C.E.) for Pitting and Deposit Corrosion at Two Levels of Carbonate/CO_2 Concentration

Solution*	Surface**	Pitting M.S. 304	Pitting M.S. 316L	Deposit M.S. 304	Deposit M.S. 316L
10:1	G	1234	1240	1130	1040
	GP	1094	1107	>770	>955
	GPP	1025	1050	>790	>1100
5:1	G	1348	1278	820	660
	GP	1111	1172	660	>925
	GPP	1143	1180	580	740
3:1	G	645	1105	520	500
	GP	1007	1040	580	985
	GPP	1130	1021	>975	>1070
2:1	G	604	617	605	530
	GP	1204	996	240	820
	GPP	1240	1103	>885	>950
1:1	G	456	420	360	340
	GP	480	890	440	440
	GPP	470	600	560	480
0.5:1	G	384	380	260	260
	GP	339	437	--	--
	GPP	--	--	--	--

*Solution — Simulated white water, 5000 ppm, total dissolved solids and containing SO_4:Cl concentrations as indicated.

**Surface — G — Regular ground through 120 grit
GP — Ground and passivated
GPP — Ground, electropolished, and passivated.

Figure 12. Margin of Safety, M.S. (mv., S.C.E.) for Types 304 and 316L Stainless Steel With Various Surface Conditions in Simulated White Water